

Promising Analytical Technologies

Denise MacMillan
Environmental Laboratory
Environmental Chemistry Branch

Long Term Monitoring Workshop
Jan 14-16, 2003
Vicksburg, MS



US Army Corps
of Engineers

Engineer Research & Development
Center

Selected Technologies

- Mass Spectrometry
- Surface Enhanced Raman Spectroscopy
- Laser Induced Breakdown Spectroscopy
- Microchip sensors



US Army Corps
of Engineers

Engineer Research & Development
Center

Performance Criteria

- Real time, fast analysis
- Highly sensitive
- Acceptable precision and accuracy
- High specificity
- Discriminate against interferences
- Achieve high signal to noise ratio
- Reliable
- Portable



US Army Corps
of Engineers

Engineer Research & Development
Center

Mass Spectrometry

- GC-Ionscan – Barringer Instruments
 - Explosives – 0.3-10 mg/kg in soil; 25-1950 ug/L in water
 - VOCs –
- Other COTS – see Syagen paper



US Army Corps
of Engineers

Engineer Research & Development
Center

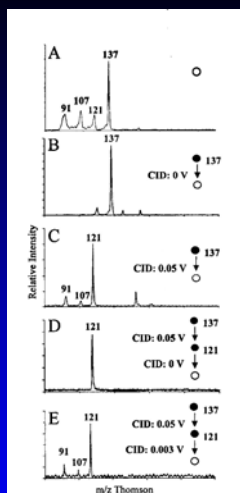
Miniature Mass Spectrometer

- Miniature Cylindrical Ion Trap – Graham Cooks, Purdue
 - 5.77 mm between end-caps; 2.5 mm inscribed radius
 - Commercial miniaturized ancillary systems
 - 55 kg
 - Battery operated
 - Tolerates high pressure
 - Inlets for water and air sampling
 - LOD = ~ 1 pg for methyl salicylate
 - Ambient temperature



US Army Corps
of Engineers

Engineer Research & Development
Center



MS/MS/MS Sequential Product Ion Scan of p-nitrotoluene

- A: Single-stage mass spectrum
- B: Isolation of molecular ion
- C: Activation of molecular ion
- D: Activation of fragment ion
- E: Collection of third generation ions



US Army Corps
of Engineers

Ritter, L. S.; Peng, Y.; Noll, R. J.; Patterson, G. E.; Aggerholm, T.; Cooks, R. G., "Analytical Performance of a Miniature Cylindrical Ion Trap Mass Spectrometer," *Anal. Chem.*, **2002**, *74*, 6154-6162.

Engineer Research & Development
Center

Miniature Mass Spectrometer

- Field-Portable, High-Speed GC/TOFMS – Syagen
 - Photoionization MS for screening followed by GC/MS
 - 12 in instrument chamber
 - 30 lbs
 - Tolerates high pressure
 - Inlets for water and air sampling
 - General LOD = ~ 2-20 pg
 - 2 min GC run with isothermal heating

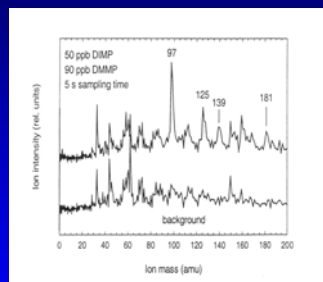


US Army Corps
of Engineers

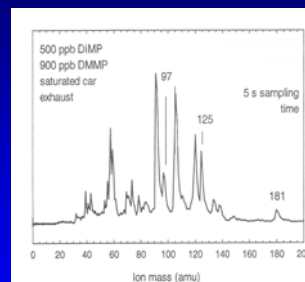
Engineer Research & Development
Center

CW Simulants in Complex Mixtures

Room Air



Car Exhaust



Syage, J. A.; Nies, B. J.; Evans, M. D.; Hanold, K. A., "Field Portable, High-Speed GC/TOFMS," *J. Am. Soc. Mass Spec.*, **2001**, 12, 648-655.



US Army Corps
of Engineers

Engineer Research & Development
Center

Surface Enhanced Raman Spectroscopy

- Analyte adsorbed onto rough metal surface



US Army Corps
of Engineers

Engineer Research & Development
Center

Laser Induced Breakdown Spectroscopy

- Laser pulse onto surface yields light-emitting plasma
- Elements give characteristic spectral features
- Fast analysis – 3 min
- Minimal, if any, sample preparation
- Small area sampled
- Simultaneous, in situ, real-time detection
- Stand-off capability



US Army Corps
of Engineers

Engineer Research & Development
Center

Fiber Optic LIBS Sensor

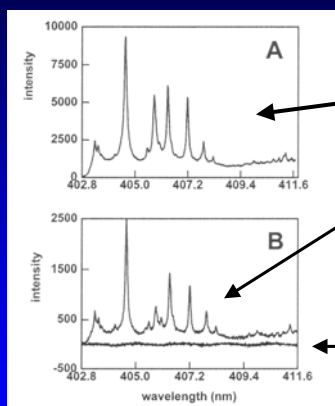
- Probe for Cone Penetrometer
- Clean site soil used as matrix for calibration
- >90% Accuracy Compared to Commercial Lab
 - Homogenized samples split



US Army Corps
of Engineers

Engineer Research & Development
Center

Lead Contamination at Camp Keller



A: Sample near surface using
initially optimized parameters

B1: Below ground sample
required newly optimized
parameters

B2: Below ground sample with
initially optimized parameters

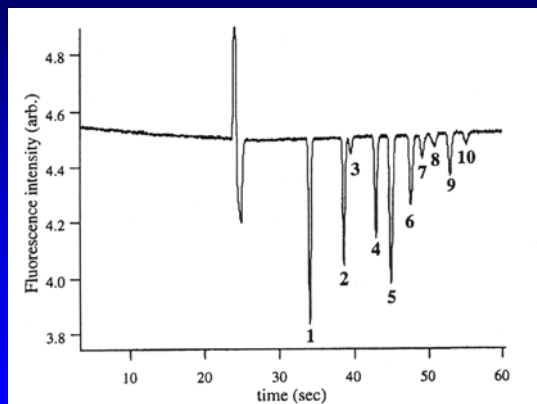


US Army Corps
of Engineers

Mosier-Boss, P. A.; Lieberman, S. H.; Theriault, G. A., "Field Demonstrations of a Direct Push FO-LIBS Metal Sensor," *Environ. Sci Technol.*, **2002**, 36, 3968-3976.

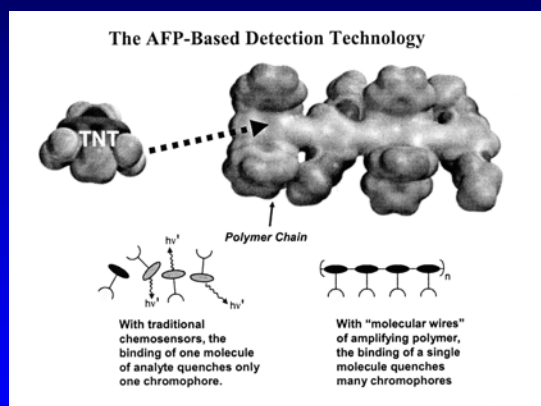
Engineer Research & Development
Center

Microchip Sensors



US Army Corps
of Engineers

Engineer Research & Development
Center



US Army Corps
of Engineers

Engineer Research & Development
Center